Handbook of instrumental techniques from CCiTUB

Secondary Ion Mass Spectrometry (SIMS): principles and applications

Francisco López

Unitat SIMS, CCiTUB, Universitat de Barcelona. Martí i Franquès, s/n. 08028 Barcelona. Spain.

email: *franlopez@ccit.ub.edu*

Abstract. This article outlines the basis of the technique and shows some examples of applications in order to exhibit the expectations of this technique in varied scientific fields.

1. Introduction

SIMS is an instrumental technique of microscopic surface analysis of composition and layer structure of solids [1-8]. It is based on the detection of emitted atomic and molecular charged particles when a material is bombarded by energetic particles.

The most important feature of SIMS is its high sensitivity for the detection of most elements of the periodic table including the lightest. Also important is the ability to distinguish isotopes, followed by a remarkable depth resolution and a large dynamic range for detection of most elements (more than 6 orders of magnitude). The combination of this set of features makes SIMS an attractive analytical method. However, as major drawback, one has to mention its difficulties for quantification because SIMS only detects the ionized fraction of the species being measured, which is difficult to evaluate in general.

The technique is of great significance in science of new materials in the fields of electronics, optics and mechanics. Within these fields it can be applied to thin layers of different materials, such as hard coatings for cutting tools, thin-film superconductors, amorphous semiconductors, thin layers of optical applications, etc. Its versatility also places it as an important analytical technique in other fields such as metallurgy, ceramics, geology, organic chemistry, biology, etc. Each of the applications of SIMS is preceded by some considerations regarding the most appropriate experimental parameters (vacuum, primary current and energy, mass resolution, sensitivity, etc.).

The different forms of embodiment of a SIMS with respect to the different types of instruments that form it create a variety of SIMS systems. Each system is optimized in a certain way that takes into account the applications that are intended.

2. Physical principles

2.1 Fundamentals

SIMS uses an energetic primary ions beam (several keV) to bombard the sample surface, resulting in the emission of ionized secondary particles (secondary ions) -the sputtering process- which are detected by a mass spectrometer. Figure 1 illustrates schematically the basic elements that make up a SIMS experiment. In Figure 2 the sputtering process is represented. The primary ions may be of various types. The available primary ions in our instrument are $O2^+$ and Ar^+.

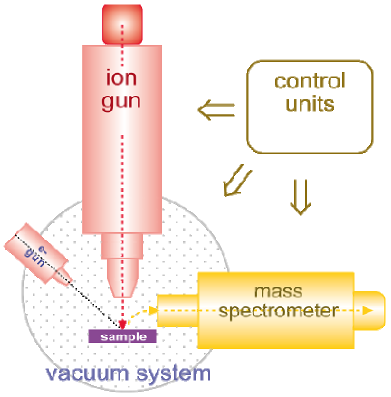

Figure 1: Basic blocks that make up a SIMS experiment.

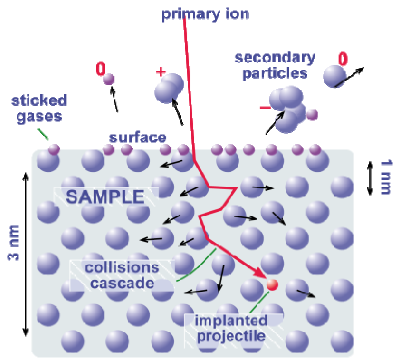

Figure 2: Illustration of the process of sputtering.

The sputtering consists in the implantation of the primary species into the sample, and the emission of surface atoms and molecules due to the energy lost by the primary species in the material [3, 6, 7, 9, 10]. The thickness of the area affected by the cascade of collisions is comparable to the primary ion path R which is given by

$$R = \int_0^E \frac{1}{dE/dx}\, dE$$

where E is the energy of primary ion, dE/dx the energy loss per unit length perpendicular to the surface. For 1 keV Ar^+ on copper, dE/dx= 100 eV/Å and R = 10 Å. A common estimate is R = 10 Å / 1 keV.

An important parameter related to the sputtering process is the atomic *sputter yield Y*, defined as the average number of atoms emitted per primary ion. The sputter yield is related to the energy transmitted by an incident ion on the target surface, or energy loss per unit length in the direction normal to the surface. For average-mass ions and 1 keV energies, Y takes values between 0.5 and 20.

SIMS is a destructive analytical technique, however, we should clarify that in most cases it requires only a small volume of material for analysis. A value of typical crater area in depth analysis is of the order of 1 mm^2. An analysis to reach 1 micron deep with an area of 1 mm^2, represent a material volume loss of 10^{-6} cm^3.

2.2 Secondary Species

As a result of the interaction of the primary beam with the sample, many new species are formed. For a given material, it is difficult to predict which secondary species will be formed and with which ionic proportions, due to the complexity of the mechanisms involved [3, 11]. In an analysis by SIMS, one can find any individual atoms that are present in the material and also any molecule that can be formed as a combination of these atoms, although many of them may have a low chance of formation or too low ionization to be detected.

Some molecules are formed inside the material before being issued as a result of the rearrangement of atoms caused by the energy deposited by primary ions, while others, may be formed out of the material near the surface by recombination of atoms and molecules once they have been emitted. Recombination is also possible with species from the residual gas molecules.

Another common problem in the detection of secondary species is mass interference, that is, different molecular aggregates with the same mass have coincident signals, and therefore, at that point the sum of all signals is measured. Some of these cases are resolved by taking as a representative signal of the element under study that corresponds to an aggregate of the atom instead of the mono-atomic ion (for example we measure $^{28}Si^{14}N$(42), instead of ^{14}N, which interfere with $^{28}Si^{+2}$ in a matrix of Si [12]).

2.3 Energy distribution of secondary ions

Secondary ions leave the sample surface with different energies following a certain distribution which has a single maximum [3, 13, 14]. The maximum is usually located at relatively low energies of the order of ten eV and depends scarcely on primary ion energy. The energy distributions have tails that can reach several hundred volts; the more complex is the molecular aggregate, the narrower is the energy distribution. The overall energy distributions depend on the ionization mechanism, the nature and energy of the primary beam, and the chemical structure of the surface.

Typically, mass spectrometers apply an electrical potential to extract ions from the area where erosion occurs, which increases the atomic number of ions collected and therefore increases the sensitivity. However, it destroys the information about the initial direction of the ion.

In common with all methods of surface analysis involving either incoming or outgoing charged particles, surface charging of insulators can be a problem. The surface potential due to charging causes a large shift on the energy distribution of secondary ions, taking it outside the energy acceptance window of the mass spectrometer and making impossible its measurement.

The charging problem requires extra equipment in order to compensate charging effects. The most common being an electron gun that sprays the measuring surface with electrons, so neutralizing positive charges. A useful method, published by the author, has been incorporated to our instrument in routine analysis in order to improve measurements conditions in insulators [15].

2.4 Quantification

As in any other analytical technique for compositional analysis, SIMS seeks to establish a relationship between measured signals and the concentration of the corresponding elements in the material; although in SIMS, this task is especially complicated. We may establish a general equation expressed as

$$I_x = Y\,\alpha_x^{\pm}\,\frac{I_p}{e}\,\beta\,C_x$$

where $\mathbf{I_X}$ = Intensity of secondary ions, **Y** = Sputter yield, $\alpha_x^{\pm}$ = Ionization factor, **β** = Transmission of the mass spectrometer, $\mathbf{C_X}$ = Concentration of element x and $\mathbf{I_P}$ = Intensity of primary ions.

The likelihood of positive ionization of the elements emitted from common matrix, exhibits a regular dependence of inverse exponential on ionization potential of the element pulled, and a similar dependence of the ionization probability of negative ions on electron affinity [6]. But there are many deviations from this behavior due to the influence of chemical and electronic states of the matrix and its interaction with the emitted ion, which makes the calculation of the probability of ionization a much more complicated problem. SIMS technique requires, therefore, carefully calibrations if quantitative results are required.

Quantification is an important issue for any analysis technique, which has led to enormous efforts to seek methods and models to convert the intensities of secondary ions into concentrations of elements present in the material [7, 16]. Today there is no single model or method of general application that allows good quantification in most SIMS analysis. Empirical or semi-empirical alternatives often give better results than theoretical models.

The use of patterns is one of such empirical methods used to obtain quantitative results in SIMS [17]. However, the diversity of possible matrices makes it a challenge to find patterns that have the same matrix effects as the sample of study. A widely used method to achieve an internal standard consists of implanting an isotope of the element of study, used as a standard in the depth profile [18].

2.5 Sensitivity

SIMS in general may be qualified as the most sensitive micro-analytical technique available nowadays. This is possible, on the one hand, because the amount of particles extracted from the material is large even in a small volume, and on the other hand, because of the high sensitivity of modern detectors that can detect the arrival of individual ions.

The sensitivity in an analysis depends on the sputter rate, Y, and the probability of ionization, $\alpha_x^{\pm}$, which will determine the minimum concentration of an element that can be detected by the spectrometer. SIMS sensitivity also depends on the transmission of the detection system, **β**. A typical value of the transmission in a quadrupole mass spectrometer type is 10^{-3}, while for a time-of-flight system is10^{-1}.

2.6 Detection Limit

The detection limit for a certain element is defined as the minimum concentration of this element that can be analyzed. A typical detection limit of SIMS is of the order of 1 ppm, although this value varies considerably depending on the element and the matrix in which it is located.

The detection limit is determined by the background intensity obtained for a given mass and a set of analysis conditions [6, 19, 20, 21]. The most important background sources in SIMS (mass interference, residual gas on the sample surface, memory effects, etc.) have been studied by many authors [3, 19, 20, 22, 23, 24, 25].

3. Methodology

3.1 Static and dynamic

When the sample is bombarded with a primary ion of high enough density, there is a significant erosion of the surface and these surface atomic layers are lost. This corresponds to the **dynamic SIMS** regime [3, 26, 27]. From the data given by the mass spectrometer as a function of time, it is possible to infer the composition of the material not only on the surface but also in depth. If the applied ion density is low enough, it will lead to a situation in which the primary ions are unlikely to affect an area previously affected by the incidence of another ion fallen before. Under these conditions, most primary ions impinge on an unexposed surface area, not previously bombarded. This situation is known as the **static SIMS** regime (SSIMS), and corresponds to a purely technical analysis of surfaces [3, 5, 7, 28]. The SSIMS condition decreases with bombarding time so the analysis must be performed in the limited time before this condition is substantially lost. The instruments implementing a SSIMS require high-transmission analyzers. Instruments devoted to SSIMS are usually highly specialized in this type of analysis and are mainly applied in organic chemistry and biology.

3.2 Bulk analysis

The easiest SIMS analysis is to make impinge a relatively focused ion beam firmly on a surface and record the secondary signals obtained in a range of masses. The ion beam produces a crater with a shape resembling an inverted Gaussian. The ions are extracted from different parts of the crater (one of the walls, some part of the bottom) and it is not possible to associate a well defined depth to each of the signals being measured. The measurement of secondary signals informs us about the composition of the material at an average depth between the surface and the bottom of the crater. This volume analysis which will be more representative of the material as a whole the more homogeneous the material in depth is. This method, although it cannot distinguish variations of elements with depth, has a very simple implementation and is useful for identifying components of a material or the presence of impurities.

3.3 Depth profile

Working in dynamic regime, secondary ions are detected from a certain depth at short intervals of time, and therefore a collection of intensities as a function of depth can be obtained. This type of measurement is called a depth profile and it is probably the most widely used method in SIMS. In practice, the signals are obtained directly in terms of bombarding time and not in terms of depth. In order to re-scale the graph from bombarding time to depth units, it is necessary to know the sputter rate $\dot{z}$ [29, 30, 31]. Figure 3 shows an example of depth profile obtained in our instrument for a diamond thin film on a Mo substrate, bombarded by $O2^+$.

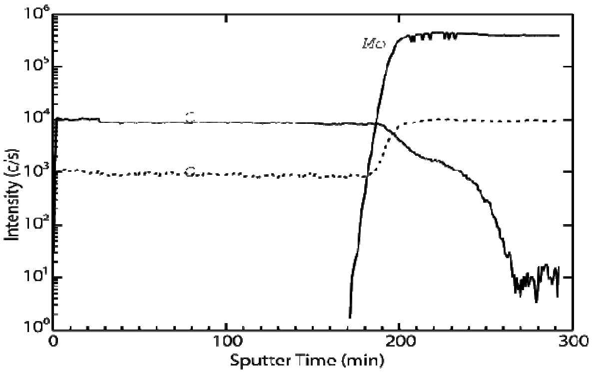

Figure 3: In depth profile obtained with our instrument on a diamond thin layer.

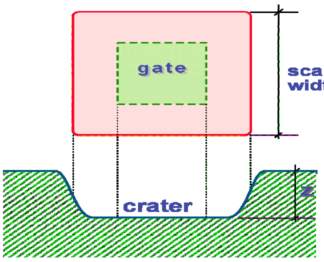

Figure 4: Main parameters in a SIMS crater squared shaped with x/y scan

To obtain reliable depth profiles, the detected species must come from a specific depth. Therefore, this technique seeks to produce a crater that has a flat bottom and consider only the species that come from this area. One way to achieve this is by scanning the primary beam so that it scrolls regularly and homogeneously a controlled area of the surface, usually square-shaped. In this way, a flat bottomed crater is obtained, although the section of the beam is not of constant ionic strength. In synchronism with the primary beam tracking, a window centered in the scanning zone that records only the ions from this area can be defined by electronic switching. Figure 4 illustrates the concepts mentioned in a square-shaped crater with swept x/y.

3.4 Dynamic range

An important feature of SIMS is its large dynamic range. This is defined as the ratio between the maximum and minimum intensities of a particular secondary species that can be measured in an in-depth profile. The minimum intensity is determined by the background signal corresponding to the secondary ion being measured, and it may depend on the element and the conditions of the analysis. The value of the dynamic range reaches more than 6 orders of magnitude for many elements depending on the species, the material and test conditions. In profiles of B implanted in Si, dynamic ranges > $5x10^5$ are obtained. This characteristic explains why SIMS measurements are usually expressed in logarithmic scale. In this representation, it is possible to see simultaneously the major and trace signals in the same graph.

3.5 Depth resolution

The atomic mixing produced by the primary ion bombardment limits the depth resolution at which elements are detected. Basically, the depth resolution depends on the mass and energy of the primary species, and their interaction with the target matrix [3, 32, 26, 6, 10]. In practice, the final depth resolution in a profile may also depend on other geometric factors such as the flatness of the crater or the roughness of the sample surface. Another factor that may be important is the roughness induced by the bombardment [24, 33].

3.6 Mass Spectrum

A mass spectrum consists of recording the intensity of a range of secondary species as a function of mass (exactly in terms of m/q). The spectrum will contain information about the elements present on the surface. A mass spectrum could be obtained after previous bombardment of the surface in dynamic regime, in order to position the primary ions at a certain depth and to know the composition of the material at a distance from the surface. Figure 5 shows a mass spectrum obtained with our instrument for a Ti alloy bombarded with oxygen primary ions. Signals of mono-atomic elements and also aggregates formed by atoms of O and Ti can be observed.

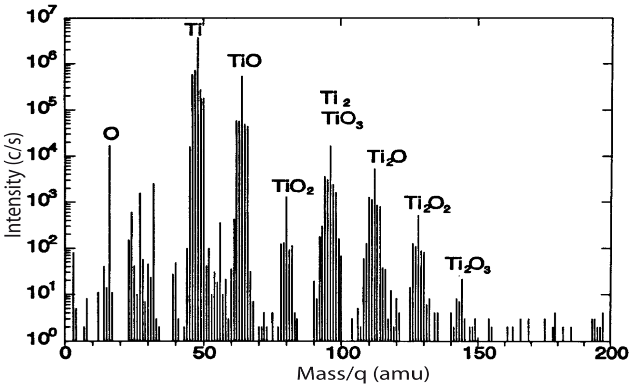

Figure 5: Mass spectrum in a Ti alloy bombarding with 0_2^+.

4. Instrumentation, ion micro-probe Atomika A-DIDA 3000-30

4.1 Presentation

The basic instrumentation required for SIMS was indicated in paragraph 1. This section briefly gives particular details of the components and characteristics of our instrument, an ion micro-probe A-DIDA3000-30 [34].

The ion micro-probe A-DIDA 3000-30 is a compact SIMS manufactured by the german company Atomika. This SIMS is of general use, relatively versatile, suitable for routine applications but mainly focused on analysis by depth profiling. It is of relatively simple structure compared with models from other companies, but with acceptable performance and versatility. The most important technical specifications of the ion micro-probe Atomika A-DIDA 3000-30 are shown in Table 1.

Figure 6: Main front view of the ion micro-probe A-DIDA 3000-30.

Figure 7: Enlarged view of main chamber

4.2 Vacuum system

SIMS experiments are carried out in ultra-high vacuum for two different reasons: firstly, to prevent the spread of primary and secondary ions along its path, and secondly, to avoid interference of the gases that are deposited on the surface to investigate. A wide variety of vacuum pumps are used such as turbo-molecular pumps, ionic, diffusion, Ti sublimation, cryogenic wall, etc. Some of them are coupled in tandem with another pump so that each one works within a suitable pressure range.

4.3 Ion gun

Our complete ion gun consists of an ion source, an ion extraction system inside of it, an acceleration system through a potential difference (0.5 to 15 kV) to determine the final energy of the beam, a system of deflectors for alignment of the beam, a focusing lens system to collimate the beam, and a deflector x/y to position the beam and to scan it. The set of ion extraction system, acceleration, deflection, alignment, focus and mass filter is called primary ion optics. Figure 8 shows a schematic diagram of the main elements that make up the A-DIDA ion gun.

Table 1. Summary of major technical specifications of the Atomika ion micro-probe A-DIDA 3000-30.

Priamary ions species	Ar^+, O_2^+
Angle of incidence	2° (almost normal)
Primary ion energy	0.5 keV to 15 keV
Primary ion current	$<10^{-10}$ A to $2x10^{-6}$ A
Densidad de corriente iones primarios	$<10^{-9}$ A/cm^2 to $2x10^{-2}$ A/cm^2
Primary ion source size	5-10 µm to 2 mm
Voltage of sample holder	[-60 V, +60V]
Beam scanning amplitud	0 to 1-2 mm energy as
Base pressure	$10^{-7} \div 10^{-8}$Pa
Extraction voltage for secondary ions	±100 V
Mass range	0-350 amu
Mass resolution at 28 amu	0.05 amu

4.4 Mass Spectrometer

The other essential part of a SIMS is the mass spectrometer, which is responsible for measuring the mass of secondary ions. In the micro-probe A-DIDA, the mass spectrometer consists of a quadrupole mass filter with a high transmission and a special secondary optics in the entry for capturing and filtering in energy the secondary ion, and a detector device for individual particles of the electron multiplier type (chaneltron). Figure 9 shows a schematic diagram of the spectrometer with the main elements.

The use of quadrupole spectrometers has some advantages such as few memory effects, few problems in the analysis of insulating materials, fast switching between modes of detection of positive and negative ions, support for easy positioning of the sample, operation and maintenance.

4.5 Computerized system

The data acquisition, program analysis and automation system are entrusted to a personal PC computer system with IEEE and RS232 standard communications. The control software has been programmed in Visual-Basic language and entirely developed by the author. The user Interaction runs in a Windows environment and the graphs and data are saved in standard ASCII format, compatible with most software applications.

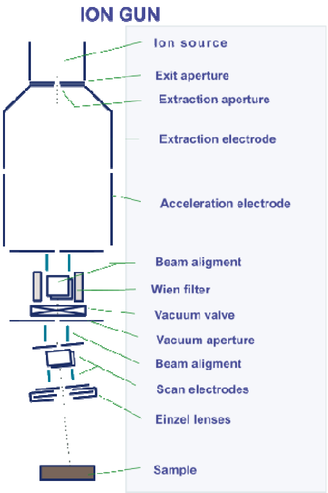

Figure 8: Schematic view of the main elements constituents of the A-DIDA3000 ion gun.

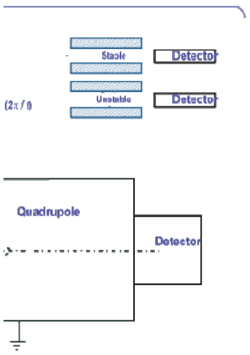

Figure 9: Schematic diagram of the quadrupole spectrometer with the main elements.

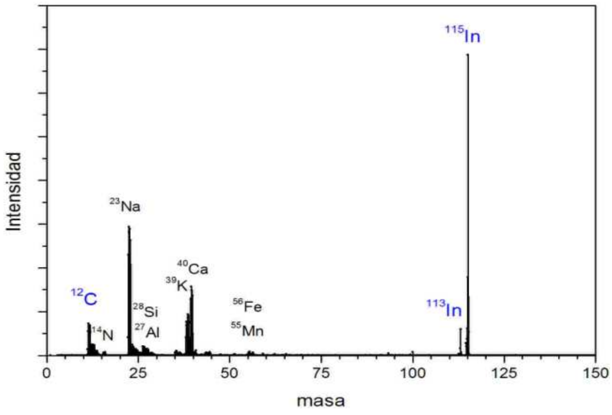

Figure 10: Mass spectrum in the metallic coating of a car emblem

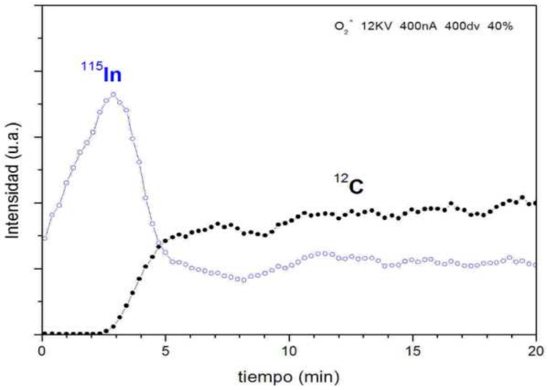

Figure 11: In-depth profile on the same sample

5. Examples of applications

The SIMS technique is applied in a wide variety of fields related with the sciences of new materials thanks to its versatility. It is an indispensable tool in many fields such as electronics, optics, metallurgy, superconductors, geology, etc. Nevertheless its biggest drawback must be indicated: the difficulty to quantify. In the following, I will show some illustrative examples of applications where our instrument has been used for the described measurements.

5.1 Analysis of the metallic coating of a car emblem

Firstly, the sample was subjected to a spectral analysis in order to identify the main components of the alloy. A mass spectrum from a mass range of 3-150 amu was performed. The result is shown in Figure 10, where the presence of In can be identified as the main constituent of the coating. Also C is detected (probably from the plastic material of the substrate) along with some contaminants.

Once In and C were identified as main elements, we planned to do a Dynamic Analysis. An in-depth profile was carried out following the In and C signals. The result is shown in Figure 11, and confirms the presence of a thin coating (≈100 nm) of In deposited on the plastic substrate.

5.2 Cathodic chromium carbide coatings

In this application, chromium carbide coatings deposited on hardened steel probes were analyzed. The coatings were obtained by cathodic arc evaporation (CAE) from chromium targets in reactive acetylene gas [35]. The effect of the deposition parameters on composition and crystalline structure was characterized by means of SIMS among other techniques. Figure 12 shows the SIMS analysis of the sample. The depth composition profiles of Cr and C reveal a good uniformity in the chromium carbide region, a sharp transition between the chromium carbide and the chromium nitride regions and a two-fold higher erosion rate for the nitride than for the carbide.

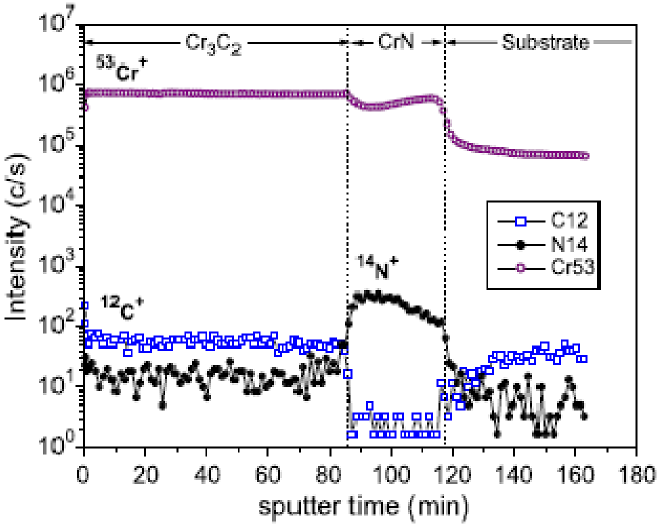

Figure 12: SIMS profile of a Cathodic chromium carbide sample: CrN (1.5 µm) + CrC (1.5 µm).

5.3 Nanometer-metal multilayer

In this work, the depth resolution (interface width) in elemental analysis and depth profiling of complex layer systems of three ion-probing techniques including SIMS was analyzed. Each technique has advantages and drawbacks [36]. From the results, it was concluded that SIMS is suitable and complementary technique for in-depth elemental analysis of metal-multilayer stacks of nm individual thickness. A very good correlation between nominal thickness and calculated values was found between the depth profiles obtained using SIMS and those obtained by other techniques, in spite of the fact that the analytical methods were very different in each case.

5.4 Nanometric chromium/chromium carbide multilayer

This example shows the analysis of metal/ceramic multilayer with periods in the nanometric range [36]. These materials have been proposed as protective coatings due to their improved tribological and mechanical properties as compared to single coatings. Secondary ion mass spectrometry confirmed the periodic multilayered structure.

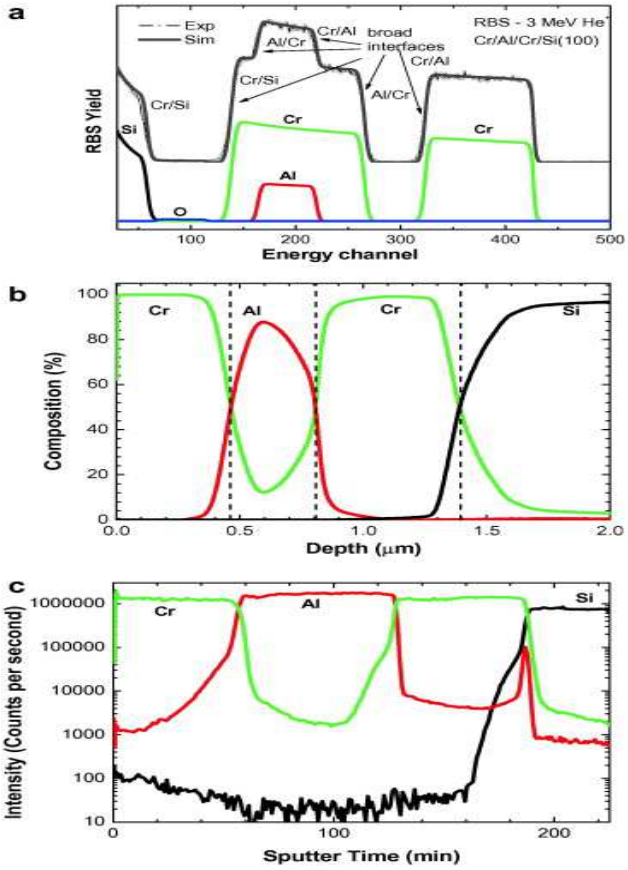

Figure 13: Depth profiles of a 450 nm Cr / 400 nm Al / 450 nm Cr tri-layer film obtained by a) Rutherford Backscattering (RBS), b) Glow-Discharge Optical Emission Spectrometry (GDOES) and c) SIMS. In a), the experimental data and the global fit have been shifted vertically from the contributions of the elemental spectra (lower part of the graphs). The dashed vertical lines in b) indicate the location of the different interfaces. Notice that, in c), the vertical axis (intensity) is in logarithmic scale.

5.5 Hydrogenated amorphous carbon films on silicon

Hydrogenated amorphous carbon films deposited on silicon by r.f. Plasma decomposition of methane were analyzed by SIMS [37].

The dependence of the Si-C transition width on substrate temperature and homogeneity of the carbon layer were studied. For films deposited on refrigerated substrates, the Si-C transition width was found to be two-fold higher than for the films deposited on unrefrigerated substrates. The secondary-ion mass spectrometry signal intensities of the main constituents are constant over the whole carbon layer (see Fig. 15). The C^{+2}-to-C^{+3} signal ratio is constant in the deep region but it increases towards the surface; this result seems to indicate that some degradation of the film occurs during the growth process.

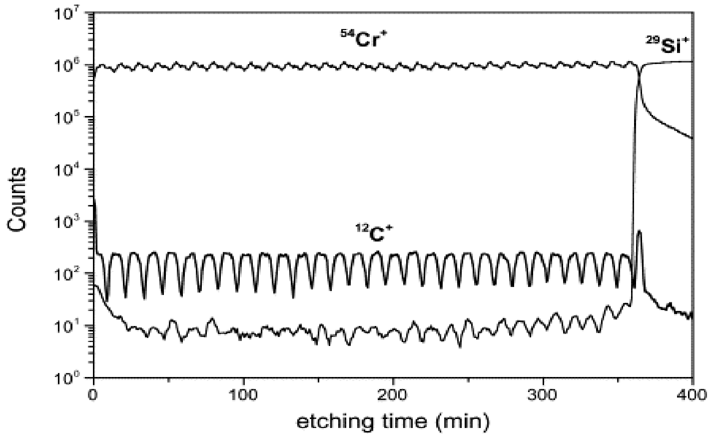

Figure 14: SIMS depth profile analysis of the 30/30 nm Cr/CrC multilayer.

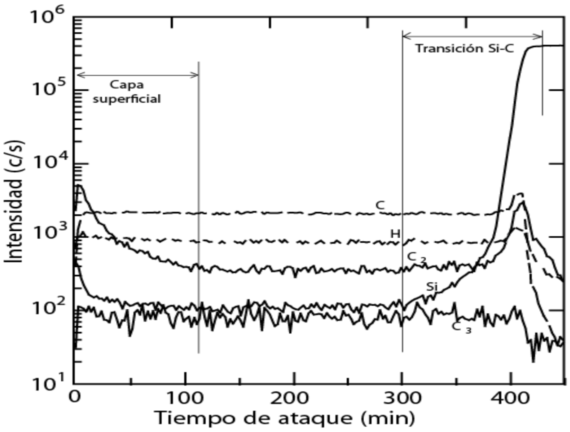

Figure 15: SIMS depth profile in the film deposited at 450 V on a refrigerated substrate.

Acknowledgments

The author wishes to thank Dr. Arturo Lousa for allowing the use of Figures 12, 13 and 14. Thanks also to Dr. Joan Esteve, Dr. María-Victoria Garcia-Cuenca and Dr. Josep Lluís Morenza, from the department of Física Aplicada i Óptica of the Facultat de Física, for their help and collaboration, and the staff of the Taller d'Electrònica and Taller de Mecànica for the services provided.

References

[1] Blattner R.J. and Evans C.A., Jr., *Scanning Electron Microscopy*, **IV**, (1980).

[2] Feldman L.C. and Mayer J.W., *Fundamentals of Surface and Thin Film Analysis*, (Elsevier, New York, 1986).

[3] Benninhoven A., F.G. Rdenauer and H.W. Werner, *Secondary Ion Mass Spectrometry: Basic Concepts*, *Instrumental Aspects*, *Applications and Trends*, (Wiley, New York 1987).

[4] Adams F., F. Michiels, M. Moens y P. Van Espen, *Analytica Chimica Acta*, **216** (1989) 25.

[5] Briggs D., A. Brown and J.C. Vickerman, *Handbook of Static Secondary Ion Mass Spectrometry*, (Wiley, New York, 1989).

[6] Wilson R.G., F.A. Stevie and C.W. Magee, *Secondary Ion Mass Spectrometry*, (Wiley, New York, 1989).

[7] Vickerman J.C, in *Secondary Ion Mass Spectrometry: Principles and Applications*, eds. J.C. Vickerman, et al.(Oxford, New York, 1989a,b,c,d,e) p. 1, p. 9, p. 35, p. 149, p. 272.

[8] Abel F., B. Agius, G. Blaise and A. Huber, en *Surfaces Interfaces et Films Minces*, ed. B. Agius, M. Froment and co-autores, (Bordas, Paris, 1990) p. 237.

[9] Behrisch R. and K. Wittmaack, in *Topics in Aplied Physics: Sputtering by Particle Bombardment III*, Eds: R. Behrisch and K. Wittmaack, Vol. **64**, (Springer-Verlag, Berlin, 1991), p. 15.

[10] Wittmaack K., in *Practical Surface Analysis* Eds: D. Briggs and M.P. Seah, Vol. **2**, (Wiley, New York, 1992) p. 105.

[11] Yu M.L. in *Topics in Aplied Physics: Sputtering by Particle Bombardment III*, Eds: R. Behrisch and K. Wittmaack, Vol. **64**, (Springer-Verlag, Berlin, 1991), p. 91.

[12] Wach W. and K. Wittmaack, Nucl. Instrum. Methods, **149**, 259 (1978).

[13] Thompson M.W., *Philos. Mag.*, **18** (1968) 377.

[14] Hofer W.O., in *Topics in Aplied Physics: Sputtering by Particle Bombardment III*, Eds: R. Behrisch and K. Wittmaack, Vol. **64**, (Springer-Verlag, Berlin, 1991), p. 15.

[15] López F., M. V. García-Cuenca, J. L. Andújar and J. L. Morenza, in: Secondary Ion Mass Spectrometry SIMS VIII, ed. by A. Benninghoven et al.(Wiley, New York, 1992), p.459.

[16] Williams P., in *Practical Surface Analysis*, **Vol.2**, eds. D. Briggs and M.P. Seah, (Wiley, New York, 1992) p. 177.

[17] Homma Y. y Kurosawa S.; Yoshioka Y.; Shibata M.; Nomura K.; Nakamura Y., *Anal. Chem.*, **57** (1985) 2928.

[18] Smith H.E. y Morrison G.H., *Anal. Chem.*, **57** (1985) 2663.

[19] Kobayashi J., M. Nakajima y K. Ishida, *J. Vac. Sci. Techonol.* **A6** (1988) 86.

[20] Kobayashi J., M.Nakajima y K. Ishida, J. Vac. Sci. Techonol. **A7** (1989) 2542.

[21] Wittmaack K., in "Sputtering by Particle Bombardment III", *Topics in Aplied Physics*, Eds: R. Behrisch y K. Wittmaack, Vol. **64**, (Springer-Verlag, Berlin, 1991), p. 161.

[22] Magee C.W., R.E. Honig and C. A. Evans, Jr., in *Secondary Ion Mass Spectrometry SIMS III*, ed. by A. Benninghoven, J. Giber, M. Riedel and H.W. Werner, (Springer-Verlag, Berlin, 1982) p. 172.

[23] Frenzel H. and Maul J. L., in *Secondary Ion Mass Spectrometry SIMS III*, ed. by A. Benninghoven, J. Giber, M. Riedel and H.W. Werner, Springer-Verlag, Berlin (1982), p.94.

[24] Hofman S. in *Secondary Ion Mass Spectrometry SIMS III*, ed. by A. Benninghoven, J. Giber, M. Riedel and H.W. Werner, Springer-Verlag, Berlin (1982), p. 186.

[25] Clegg J.B., in *Secondary Ion Mass Spectrometry SIMS V*, ed. by A. Benninghoven, R.J. Colton, D.S. Simons and H.W. Werner, Springer-Verlag, Berlin (1986), p. 112.

[26] McPhail D.S., in *Secondary Ion Mass Spectrometry*, eds. J.C. Vickerman, A. Brown and N.M. Reed, (Oxford, New York, 1989) p.105.

[27] Dowsett M.G. and E.A. Clark, in *Practical Surface Analysis* Eds: D. Briggs and M.P. Seah, Vol. **2**, (Wiley, New York, 1992) p. 229.

[28] Briggs D. in *Practical Surface Analysis* Eds: D. Briggs and M.P. Seah, Vol. **2**, (Wiley, New York, 1992) p. 367.

[29] Kempf J.E. and Wagner H.H., in *Thin Film Depth Profile Analysis*, H. Oechsner, Springer-Verlag, Berlin (1984) p. 87.

[30] Kirschner J. and H.-W. Etzkorn, in *Thin Film Depth Profile Analysis*, ed. H. Oechsner, (Springer-Verlag, Berlin, 1984) p. 103.

[31] López F., M.V. García-Cuenca, J.M. Asensi and J.L. Morenza, Applied Surface Science, Volumes 70-71, Part 1, 2 June 1993, Pages 68-72.

[32] Meuris M., Vandervorst W., De Bisschop P. y Avau D., *Appl. Phys. Lett.*, **54** (1989) 1531.

[33] Vajo J.J. y Cirlin E.-H., Wilson R.G. y Hasenberg T.C., en *Secondary Ion Mass Spectrometry SIMS VIII*, Wiley (1992).

[34] Maul J.L. y Frenzel H. in *Ion Implantation Techniques*, ed. by H. Ryssel y Glawischnig, Springer-Verlag, Berlin (1982), p.361.

[35] Esteve J., J. Romero, M. Gómez, A. Lousa., Surface & Coating Technology, 188-189 (2004) 506-510.

[36] Escobar R., R. Gago, A. Lousa and J.M. Albella, Trends in Analytical Chemistry, Vol. **28**, No. 4, 2009.

[37] Romero J., A. Lousa, E. Martınez and J. Esteve, Surface and Coatings Technology, 163 – 164 (2003) 392–397.

[38] López F, M.V. Garcia-Cuenca, C. Serra and J.L. Morenza, Diamond and Related Materials, Volume **2**, Issues 2-4, 31 March 1993, Pages 229-232.